

ART. XXII.—*Flotation of Minerals.*

PART II.

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As stated in my paper read before this Society in December, 1910, the various flotation processes which are now being so largely used for separating metallic sulphides from sulphide ores depend upon differential gas and liquid attaching phenomena. The sulphides are floated (on aqueous solutions) as a sort of scum or froth by the agency of either gases alone or by gases assisted by small proportions of various oily substances. The paper referred to contained the results of investigation bearing on these gases and liquid attaching phenomena, and the present paper deals with a continuation of this work.

**The attachment of gases and liquids to solids
and to each other with special reference
to flotation processes.**

As oils and other substances of an oily nature are being extensively used in these processes, the behaviour of these substances under varying conditions was investigated.

In a paper¹ by Lord Rayleigh it was shown that the presence of small proportions of various contaminants in water very materially affected its frothing properties. Pure water on being vigorously agitated with air shows very little tendency to produce a froth. This tendency is very much increased by the

1 "On the tension of water surfaces clean and contaminated." Phil. Mag. xxx., Nov. 1890, pp. 386-400.

"Experiments with surface films." Phil. Mag. xxxiii., 1892, pp. 363-373.

"On the theory of Surface Forces: Effects of slight contaminations." Phil. Mag. xxxiii., pp. 468-471.

"Investigations on Capillarity." Phil. Mag. xlviii., 1899, pp. 321-337.

addition of small proportions of some substances, as saponine and acetic acid. These contaminants include not only substances which are soluble in water, such as saponine and acetic acid, but substances which are insoluble in water, such as various oils and certain finely divided solid substances.

Without doubt liquid cohesion and attachment effects are important factors in determining froth producing variations, but it seems apparent that gas attachment is the chief factor, and a comparison of the various proportions of froth produced would therefore afford an approximate measurement of the attachment of air to water and to various aqueous solutions and mixtures.

The following list shows the order in which a series of various substances came in their froth producing effects. In each case one drop of the contaminant was mixed with 60 c.c. of pure water and agitated vigorously with air, the froth produced being noted:—

1. Saponine (greatest froth).
2. Turpentine.
Phellandrene.
Residual oil (from rectification of eucalyptol).
3. Tasmanian refined petrol (0.754).
Acetic acid.
4. Eucalyptol, crude shale oil (0.900).
Cotton seed oil.
5. Oleic acid.
Combustion engine oil (0.831).
6. Tasmanian shale residual oil.
Tasmanian shale turps. substitute.
Austral machine oil.
7. Kerosene.
8. Alcohol, oil of winter-green, naphtha, gasolene, ether (petroleum), ether (sulphuric).

The froth produced by the last contaminants in the series was practically the same as with pure water.

With the view of obtaining some confirmation of the above series of results the following experiments were carried out:—

1. Agitation with air, 60 c.c. of water and 10 c.c. of the various contaminants.

2. Agitation with air each of the various contaminants alone. The results of these experiments are given below :—

Agitation with air and 60 c.c. of water and 10 c.c. of each of the contaminants :—

1. Saponine (most persistent froth).
2. Naphtha.
3. Kerosene.
4. Austral machine oil.
5. Oleic acid.
6. Turpentine.
7. Phellandrene.
8. Eucalyptol.
9. Gasolene.
10. Alcohol.
11. Acetic acid.
12. Glycerine (practically no froth).

Agitation with air, each of the various contaminants alone :—

The order in this instance is practically the same as that in the series where one drop of the contaminant to 60 c.c. of water was used. The froth produced is, however, less than when the water is present.

It is difficult to reconcile these three series of results. The variations may be due to the varying gas and liquid attachments under the different conditions.

It being apparent that the opacity of the various mixtures of oil and water after agitation would afford some indication of the measure of attachment of one to the other, the following series of opacity observations were made.

In each case one drop of the contaminant was added to 60 c.c. of water and agitated with air, and after standing the opacity of the solution due to the emulsion formed was observed.

1. Oil of winter-green : greatest opacity.
2. Turpentine, cotton-seed oil.
3. Residual oil from rectification of eucalyptol.
4. Austral machine oil.
5. Phellandrene.
6. Kerosene.
7. Naphtha.

In the case of the other substances a clear solution resulted.

These solutions in some cases still showed opacity after standing for a week.

When 10 c.c. of the substance was added to 60 c.c. of water and agitated with air, after standing for some time, a layer of white emulsion was noticed between the layer of oil and the surface of the water. This was greatest in the case of machine oil and oleic acid.

The following list gives the order in which the various substances come with regard to the amount of emulsion formed:—

1. Machine oil and oleic acid.
2. Oil of winter-green.
3. Naphtha.
4. Kerosene.
5. Eucalyptol.
6. Turpentine.

The other substances showed no emulsion.

In the case of oil of winter-green, the emulsion occurred on the top of the oil, which, being heavier than water, sank to the bottom of the measuring cylinder.

In conducting these tests with oils and water, it was noticed that some oils at once spread out to form a film over the surface of the water, while others remain in the form of a globule.

Some of the light thin oils when added as a drop to a large surface of water will spread out in a very thin film to such an extent that the iridescence disappears in the centre of the area.

The following oils spread out as a thin film on the surface of water when the oil was added as a drop to the water:—turpentine, phellandrene, gasolene, naphtha, eucalyptol, kerosene. Oleic acid formed a film with one drop, but on adding another drop, the second remained as a globule.

The following oils remained as globules on the surface of the water:—cotton seed oil, machine oil, engine oil.

This property of oil depends apparently to a large extent on the viscosity of the oil, for as a rule, and with the thin oils, a film was formed, and with the thicker oils the drop remained as a globule. Viscosity is not, however, the only determining factor, as some of the more viscous oils were found to form films, and some interaction between the surfaces of the oil and water must take place.

The adsorption of oil by minerals.

The effect of oils has long been known in protecting minerals from being wetted by water, owing to the oiling of their surfaces, and also the affinity of oils for metals and many metallic substances. As no accurate method of measuring this affinity or attraction has suggested itself, and as minerals may occur in many different forms with varying physical characters, no attempt is made here to make a definite classification on this basis. Tests were, however, carried out to show the amount of oil absorbed by minerals, and the character of the resultant product.

Mixtures of the mineral to be tested, water, and oil (with and without a small quantity of acid) in definite quantities were taken and agitated thoroughly till the character of the resultant product became constant.

The results of these tests showed that while there are undoubtedly differences in the degree of attraction between a given sulphide and various oils, and between various sulphides and a given oil, the general behaviour between various sulphides and various oils in the presence of water is practically the same in character, i.e., all sulphides will become attached to all oils in preference to water. With the silicates and other rock minerals usually found in the gangue material of ores, the character of the product varies with different minerals.

In the case of sulphides, bottles were taken containing 200 c.c. water, 5 gms. of the oil being used, and 0.5 gm. sulphuric acid. Increasing amounts of the sulphides were added to each bottle, and well agitated to bring the mineral into intimate contact with the oil.

The following is a summary of the results obtained from these experiments:—

In acidulated solution.

In the first test zinc blende crushed to pass a 40-mesh sieve was used with a heavy engine oil.

The contents of the bottles were as follows:—

Water, 20 c.c.; oil, 5 gm.; sulphuric acid, 0.5 gm.

To No. 1 bottle, 1 gm. of the mineral was added.

„	„	2	„	5	„	„	„
„	„	3	„	10	„	„	„
„	„	4	„	20	„	„	„
„	„	5	„	30	„	„	„
„	„	6	„	40	„	„	„
„	„	7	„	80	„	„	„
„	„	8	„	120	„	„	„

If any intermediate or greater quantity of mineral was needed to fix a certain point, e.g., 60 or 200 gms., another bottle was added to the series as required.

With the proportion of 1 gm. blende to 5 gms. oil, on agitating, some of the blende floated on the solution, being buoyed up by the oil and entangled air bubbles. On standing, all the mineral sank to the bottom of the bottle, carrying large "blobs" of oil with it. The product formed by the oil and blende was oily and non-miscible with the solution. An excess of oil floated on the surface of the solution and adhered to the surface of the glass above the level of the solution.

With 5 gms. blende much oil was carried down with the blende, but on standing some of it broke away and came to the surface of the solution again, leaving an oily mass non-miscible with the solution. An excess of oil showed on the surface and adhering to the glass above the level of the solution.

With 10 gms. a heavy, freely flowing oily magma was formed below the solution. The excess of oil still showed on the surface of the solution.

With 20 gms. of the blende the oily product became more putty-like in appearance, and moved less freely than with 10 gm. An excess of oil still showed on the surface of the solution and on the bottle.

With 30 gms. a putty-like plastic mass was formed by the blende and oil, which was very difficult to break up on agitation. A slight excess of oil still showed on the surface of the solution.

With 40 gms. the product broke up into large rounded lumps on agitation. No excess of oil showed on the surface of the solution or on the bottle. On violent agitation a few bubbles of air became attached to the mass.

With 80 gms. the product of the oil and blende consisted of a mass of small coherent aggregations, which on violent agitation attached many air bubbles, but which would not float the mineral.

With 120 gms. the aggregates of blende and oil were smaller and less coherent. The zinc blende at this stage seemed more prone to attach air bubbles, and showed a tendency to float.

The appearance of the product was quite different from a similar quantity of unoled blende in water.

Another series on the same lines as the above, using galena and oleic acid in similar proportions to the blende and engine oil, showed that the general character of the products was similar to those produced with blende and engine oil.

The oily magmas on the bottom of the bottles formed by the galena and oleic acid were less viscous and flowed more freely. A little free oil still showed on the surface of the water when 40 gms. galena had been added. No free oil showed with 80 gms. The products with 80 gms. and 120 gms. galena were more coherent and less prone to attach bubbles of air than was the case with zinc blende. The stage at which the small granules formed was less marked with the galena than with the blende.

In another series with heavy lubricating oil and zinc blende, most of the oil was carried down to the bottom in the form of a putty-like ball with the blende when 30 gms. of the latter had been added. This plastic mass would not break up on shaking violently, and was not miscible with the solution.

With 20 gms. of the blende and the oil, the product was a thin plastic mass on the bottom of the bottle, and non-miscible with water. A large excess of oil showed on the surface of the water.

With 40 gms. of blende, the mass or magma showed a tendency to break up into small lumps, but showed no tendency to attach air bubbles. The lumps were rounded and were about the size of broad-beans. No free oil showed on the surface of the water.

In another series using copper pyrites and 5 gms. heavy engine oil, all the oil was carried down with 30 gms. of the copper pyrites, to form the putty-like magma which would not break upon agitation.

When 40 gms. had been added the magma showed a tendency to break up on agitation into smaller lumps, but showed no tendency to attach air bubbles.

With 80 gms. of copper pyrites the product formed was a mass of coherent aggregates under the solution, each aggregate being about the size of fishes' roe.

With 120 gms. many air bubbles became attached, and a marked tendency to float was shown. The aggregates were smaller than when 80 gms. of copper pyrites had been added.

With galena and kerosene all the oil was not carried down till 80 gms. had been added. The products were less coherent and less viscous than with the thicker oils.

With galena and petrol a considerable excess of oil showed on the surface of the water when 40 gms. of the galena had been added.

Using machine oil with galena, very little excess of oil showed on the surface when 30 gms. galena had been added, and no excess showed with 40 gms. With 60 gms. galena the magma showed a tendency to break up on shaking and to attach air bubbles.

With 5 gms. cotton seed oil and galena a small excess of free oil appeared on the surface of the water when 30 gms. galena had been added. No excess of oil showed with 40 gms. galena. The putty-like magma formed, but was not so viscous as with the thicker oils. No distinct stage occurred at which the oily magma broke up into smaller rounded lumps, as in the case with some of the oils.

With 60 gms. a tendency to attach air bubbles was shown by the magma, and when 80 gms. galena had been added some of the galena would float on agitation.

Using a eucalyptus oil containing 80 per cent. phellandrene, it was not till 80 gms. of the galena had been added that all the oil was carried down. No distinct "putty" stage occurred, all the oily products being more or less like a freely moving pulp.

A series on the same lines as the above tests, but using minerals that had been "sized," was then tried. Some galena crushed to pass a 30-mesh (linear inch) sieve, but retained on a 40-mesh, was mixed with water and 5 gms. oleic acid, as in the other tests.

With 80 gms. galena a slight excess of oleic acid still showed on the surface of the water. All the oily products under the surface of the water were feebly coherent, but no distinct putty stage occurred. With 200 gms. galena a few air bubbles became attached.

Using galena crushed to pass an 80-mesh, and retained on a 120-mesh sieve, with 5 gms. oleic acid, all the oil was carried down with 60 gms. of the mineral to form the characteristic putty-like magma. A very small excess of oil showed on the surface of the water with 40 gms. of galena.

With galena crushed to pass 120-mesh sieve all the oil was carried down by 40 gms. of the mineral. When 30 gms. had been added, the plastic putty-like mass was formed. With 120 gms. of this sized galena to 5 gms. of the oleic acid, the product of the galena and oil was much less coherent than with 120 gms. of the galena crushed to pass an 80 and remaining on a 120-mesh sieve.

In water without the addition of acid.

The foregoing tests were carried out with water acidulated with 0.5 gm. sulphuric acid. The following is a short summary of the results of tests on the same lines, but using water which had not been acidulated.

Using galena crushed to pass 120-mesh sieve and 5 gms. of waste engine oil (fairly thick), the same general results were obtained as when acid was present. All the oil was carried down with 30 gms. of the galena. The putty-like magma occurred when 40 gms. had been added, this product being firmer than that formed with 30 gms.

When 60 gms. of galena had been added the magma broke up into granules. With 80 gms. of galena, air bubbles showed a tendency to become attached, and with 120 gms. galena a marked tendency to float on agitation was observed.

Other tests on the same lines without acid showed that with smaller proportions of oil to mineral the product was more prone to attach air bubbles and had a more flocculent appearance than when acid was present.

Two bottles containing 50 gms. galena and 0.8 gm. oleic acid with 200 c.c. water were taken, and to one of them 0.5 gm.

sulphuric acid was added. The appearance and character of the products formed after agitating vigorously differed from one another. The aggregations formed in the acidulated solution were less flocculent and showed less tendency to float on agitation.

Silicates and other gangue minerals:—*In water.*

The various silicates and other gangue constituents of sulphide ores when agitated with various proportions of oil and an excess of water exhibit a lesser tendency to attach the oil than the various metallic sulphides. This tendency to attach oil in preference to water is very small in the case of the more acidic minerals, and so great in the case of the more basic minerals that their behaviour approaches that of some of the metallic sulphides. For instance, with 40 gms. of quartz or orthoclase feldspar, 5 gms. of oleic acid and 200 gms. of water, nearly the whole of the oil will separate and float on the surface of the water, and the mineral particles sink in the water without any sign of aggregation, a few scattered blobs of oil only being carried down with the mineral. On the other hand, with similar proportions of rhodonite and garnet, oil and water, the minerals unite with the oil to form coherent aggregations, and no oil separates as in the case of quartz and feldspar.

Calcite also produces coherent aggregations with oil which, on agitation, readily attach air bubbles.

In acidulated solutions.

The addition of small proportions of acid (0.5 gm. sulphuric acid) to the water in all cases lessens the oil attachment. For example, on agitating the above proportions of quartz and oleic with acidulated water the quartz behaves as if no oil were present. This is also the case with orthoclase feldspar.

With rhodonite and oleic acid, with acidulated water in the same proportions as before, free oil separates and floats on the surface of the solution. The product is a sandy pulp which is freely miscible with the solution. This pulp has an appearance very different from the product formed with the non-acidulated water, oil and rhodonite in the same proportions. With mix-

tures of galena and rhodonite, the oil collects the galena to form granules, and the rhodonite remains as a sandy pulp which could be washed out if desired. In cases of a mixture of a sulphide which will attach oil and a gangue mineral which, in an acidulated solution, will not attach oil, some of the gangue mineral is held mechanically by the sulphide aggregates, and thus may be caused to float, although having no natural tendency to do so. In such a case, what may be termed coadsorption may take place. For example, quartz sand by itself will not float with oil in a non-acidulated solution, but the particles of quartz sand in a gangue with other minerals, as in the case of Broken Hill tailings, are readily floated with oil in non-acidulated water. This coadsorption will take place in feebly acid solutions, and thus particles of rhodonite and other gangue may be caused to float.

From the above tests the following may be deduced:—

Adsorption of oil in water.

1. Finely divided sulphides when suspended in water will adsorb varying amounts of oil. Large proportions of oil tend to form magma, and smaller proportions plastic masses and coherent aggregates. The character of these oily magmas depends upon the amount and the character of the oil used. Thick oils give viscous coherent products, and thin oils give less coherent products. Oily magmas containing considerable proportions of oil will entangle and hold gaseous bubbles with a degree of persistence which depends on the viscosity of the oil.

Sulphides carrying an adsorption of about 5 per cent. of oil tend to attach gaseous bubbles, and this tendency increases as the proportion of oil diminishes, until a certain limit is reached which is 0.5 per cent. or thereabouts.

2. The adsorption is more pronounced with sulphides than with such minerals as quartz, felspar and most of the acidic rocky minerals forming the gangue of ores.

3. Some of the silicates and other gangue forming minerals will adsorb oils in a manner approaching that of the sulphides, for example, rhodonite, garnet, magnetite and calcite.

4. As shown by the tests on sized minerals the amount of oil adsorbed depends upon the extent of surface exposed.

In acidulated solutions.

1. The sulphides will adsorb oil in the same manner to form oily magmas, plastic masses and coherent aggregations, as in the case of water and oil without acid. The amount depends on the extent of surface exposed by the minerals, as previously.

2. The gangue minerals will not adsorb oils to nearly the same extent as when no acid is present.

3. The maximum amount of oil adsorbed by sulphides in a stable manner when crushed to pass through an 80-mesh sieve (linear inch) is in the neighbourhood of 10 to 15 per cent. of their weight. This is shown by the absence of excess of oil on the surface of the solution in the above tests when the percentage of oil to mineral was at or near these values. The tendency of the plastic magma to break up and form less coherent aggregates at this point also indicates this limit of true adsorption.

Conclusions.

When finely divided metallic sulphides are vigorously agitated with an excess of water and a small proportion of oil, the oil is adsorbed by the sulphide particles. As shown by the previous tests on the sized material, the quantity of oil adsorbed depends upon the extent of the surface exposed. This being so, it seems safe to assume that the adsorbed oil is evenly distributed over the surface of the particles. When the quantity of oil adsorbed is very small, the general appearance of the sulphide does not differ from that of unoled particles. With a sulphide such as galena, which has been crushed to pass through an 80-mesh (linear inch) sieve, this point of apparent difference is reached when the proportion of oil adsorbed (in the case of oleic acid) is between 0.05 and 0.10 per cent. Even with these small proportions, various physical tests indicate that the particles are oiled. This can be shown by their aversion to become wetted by water, and by the fact that the odour of decomposed oil is noticed on heating.

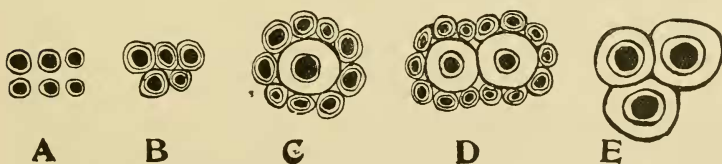
Such a quantity as 0.1 per cent. cannot be separated by squeezing, centrifugal force or other mechanical means, and any such quantity of adsorbed oil as 0.1 per cent. may be regarded as a

true adsorption of the oil by the mineral. When more oil is added it is probable that a secondary envelope of oil becomes attached to the primary film. When this oil film is thin, there is still the attraction of the oil for the sulphide, but as the film becomes thicker the subsequent overlapping envelopes of oil are held by the attachment of one oil film for another. These overlapping films are less persistently held than the primary films, and some of the oil can be separated mechanically, as by pressure or centrifugal force. The point at which the secondary film is thickest and still stable is represented in the above tests, when no excess of oil shows on the surface of the solution.

The various stages between the primary adsorption and the putty-like product represent the gradual thickening of the secondary oil envelope. The strength of the attachment of the secondary film depends largely on the cohesion of the oil itself, the more viscous oils forming more coherent products and the thinner oils less coherent products.

In the test on sized galena crushed to pass an 80 sieve but retained on a 120-mesh sieve (linear inch), it was found that all the oil (5 gms. oleic acid) was adsorbed by 60 gms. of the galena. From these data, the approximate thickness of the oil film at this stage in the adsorption can be calculated. Assuming that the average size of the particles is $\frac{1}{100}$ inch, and that the particles are cubes, the thickness of the oil film would be 0.003 centimetre.

Diagrammatically these successive oil attachments may be shown as follows:—



Diagrammatic representation of oil adsorptions showing the gradual thickening of the secondary film of oil from the primary adsorption to the oily magma. The concentric rings represent the oil films round the mineral particles.

- A Primary adsorption—no cohesion of particles.
- B Secondary attachments—cohesion.
- C Greater cohesion—forming small aggregates.
- D Larger aggregates.
- E Oily magma—all the interstitial spaces filled with oil.

Analogy of oil adsorptions with water adsorptions.

Oil attachments and water attachments present many similarities. A sulphide carrying 2 or 3 per cent. oil cannot be deprived of its oil by gravity, centrifugal force or other mechanical means. Similarly in the case of wet sand carrying a similar proportion of water, the water cannot be readily separated mechanically. In both cases with the small attachments the laws of gravity are not obeyed. With larger proportions the oil and water will separate out by gravity.

There is also a similarity between the gradual wetting of a finely crushed mineral with water, from the feebly coherent damp mineral to the thick coherent pulp, and the feebly coherent sulphide with a small proportion of oil to the various stages of oily magma. Whether the mineral particles are feebly coherent, due to the presence of a small quantity of water, or when under the surface of a solution the mineral particles are feebly coherent, due to the presence of a small quantity of oil, in both cases the interstitial spaces remain unfilled, in the first case with water and in the second with oil.

In the presence of excess of water and when the mineral has adsorbed as much oil as it will, the interstitial spaces become filled with the respective liquids to form coherent pulp or magma.

Gas attachments.

In my previous paper it was shown that mineral particles would adsorb gases to an extent not previously suspected, and that they would retain the gas adsorptions with such a persistency that they could neither be easily separated by mechanical means nor much affected by gravity and gas expansion. It was also shown that in the case of adsorptions consisting of a mixture of gases, the respective gases may be separated fractionally,

the law of gaseous diffusion apparently not being obeyed. With the view of further investigating these gas adsorption phenomena, the following series of experiments were conducted:—

1. Pieces of copper and silver foil were cleaned by boiling in a solution of sodium hydroxide, washing in distilled water and drying. These cleaned pieces of foil and similar uncleaned pieces of foil were then placed in a vacuum flask together with (a) ordinary distilled water, (b) air-free distilled water, (c) ordinary tap water, and subjected to a reduced pressure (26 inches mercury), with the following results:—

	Distilled Water.	Air free Distilled Water.	Tap Water.
Cleaned Foil	A few bubbles collected on the foil, but the foil does not float.	Very few bubbles formed on the foil; when these were detached no more formed.	Foil floats by the buoyancy of the bubbles that become attached.
Uncleaned Foil	Many bubbles become attached and the foil floats to the surface.	A few bubbles form on the foil, on detaching which no more formed.	Same as cleaned foil.

On repeating these experiments with the various waters to which a drop of oleic acid had been added and agitated, in all cases the cleaned and uncleaned foil collected gas bubbles. The uncleaned foil floated and remained floating, but the cleaned foil came to the surface repeatedly but did not remain floating. These experiments show that the persistency of the attachment of the gas bubbles is increased when the surface of the foil is contaminated with some oily substance.

2. Six steel needles were boiled in strong sodium hydroxide solution for half an hour, washed with distilled water and allowed to stand in absolute alcohol for half an hour. They were then dried in a desiccator. The needles would not then float on freshly drawn distilled water. When the water was allowed to stand for some time in an evaporating dish, exposed to the air, it was found that they would float.

Another set of needles and pieces of iron wire similarly cleaned would not float at first, but on being kept in a desiccator for two days would float on the surface of distilled water. Similarly some particles of sulphides when washed with alcohol would not float, but on exposure for some time floated. With a preliminary wash in dilute sulphuric acid prior to the other cleansing, the behaviour of the needles and wire was the same as in the case of the other method of cleansing.

This preliminary treatment would remove any oily matter present. When the needles were dried by the aid of a lens and the sun's rays, their floating properties seemed to be improved. If the needles were handled they were found to float much more readily, becoming greasy by contact with the fingers.

These experiments show that perfectly cleaned needles and iron wire will float on the surface of distilled water under the following condition, viz., (a) if the water is allowed to stand for some time in contact with the air, (b) if the needles and wire are allowed to remain exposed to the air for sufficient time.

In the first case probably a layer of fine dust collects on the surface of the water, and in the second case probably the attachment of the air becomes greater after a certain time has elapsed.

3. Cleaned and uncleaned pieces of iron wire on being immersed in a saturated solution of carbon dioxide showed the following results, respectively:—

The cleaned pieces collected very few bubbles on their surface, and the uncleaned pieces were at once covered with a frost of bubbles, and caused to float to the surface. If one of the cleaned pieces is rubbed between the fingers it behaves similarly to the uncleaned wire, and is caused to float. These experiments also show that the gas attachment is enhanced by the presence of some oily material on the surface of the metal.

In order to compare the amount of gas given off from oiled and unoled surfaces the following test was carried out:—Two cubical pieces of galena of approximately the same size with the same extent of surface exposed were taken, one of which was greased with a very small amount of vaseline. The two pieces of galena were then placed under inverted separating funnels

filled with a saturated solution of carbon dioxide and standing in a basin of the same solution. Bubbles of carbon dioxide gas were at once evolved from both pieces of mineral. The bubbles on the oiled fragment grew to a larger size, and were held more tenaciously, but more gas was given off from the unoiled piece, as could be directly measured by the amount of solution displaced in the funnel.

These results show that the oil probably acts as an agent by which the gas bubbles are more tenaciously attached, but that it is the mineral itself which in the first place determines the gas attachment.

4. Some Broken Hill jig tailings were treated with dilute sulphuric acid, and afterwards with water, to separate the whole of the acid. On immersing in a saturated solution of carbon dioxide, bubbles of carbon dioxide gas collected on the sulphide particles, but except in the case of a few garnet particles, they did not collect on the gangue. On dealing similarly with the same tailings without the acid treatment, bubbles of carbon dioxide collected on all the particles, there being no marked distinction between the sulphide particles and the gangue particles. This shows that the acid treatment tends to prevent gas attachment in the case of the gangue particles, while it does not to the same extent similarly prevent gas attachment in the case of the sulphides.

5. Some of the flotation product produced at one of the Broken Hill mines by agitating zinciferous tailings with an acidulated solution, and a small proportion of oleic acid, were collected, as it came to the surface of the solution. This product was collected in a bottle until the bottle was completely filled, thus displacing the air. The bottle was then stoppered, and the gas contained in the flotation product gradually became disengaged as the sulphide settled down. An analysis was made of this disengaged gas, with the following results:—

(1) Analysis of gas disengaged from first sample:—Nitrogen, 72 per cent. ; oxygen, 2 per cent. ; carbon dioxide, 26 per cent

(2) Analysis of gas disengaged from second sample:—Nitrogen, 82 per cent. ; oxygen, 2 per cent. ; carbon dioxide, 16 per cent.

These samples were taken at different stages in the concentrating operation.

A sample was also obtained of a flotation product produced by a process using acidulated solution without the addition of oleic acid. The material being treated in this case was Broken Hill slimes, which had been given a slight roast to oxidise the lead sulphide to sulphate in order to prevent the latter floating. An analysis of the disengaged gas from this flotation product (the sample being obtained similarly to the previous flotation product) was as follows:—Nitrogen, 96 per cent. ; oxygen, 1 per cent. ; carbon dioxide, 4 per cent.

6. The flotation product (mentioned in paragraph 5), in which the zinc concentrate was produced by a process using a dilute acid solution and a small amount of oleic acid, was then treated as follows:—Some of the concentrate, after being deprived of all visible gas by allowing to settle, was placed in a small flask. The flask was nearly filled with the sulphides, and allowed to stand, the slight excess of solution being drawn off. This solution was faintly acid to litmus. The flask was then filled with air-free distilled water, and connected to a vacuum pump, all the connections being also filled with air-free water. On lowering the pressure in the flask the concentrates were noticed to swell up, and completely fill the flask, and an evolution of gas was at once apparent. This gas was collected and analysed. The volume was 1.7 c.c., and consisted of 58.8 per cent. carbon dioxide, 27 per cent. nitrogen, and 14.1 per cent. oxygen. The flask was then immersed in water, which was brought to the boiling point, at the same time continuing the exhaustion by means of the vacuum pump. An additional volume of 8.9 c.c. of gas collected, consisting of almost entirely carbon dioxide. The weight of the concentrates experimented with was 70 gms.

A sample of the second product referred to in paragraph 5 was then taken and similarly treated, except that the wet concentrate was made slightly alkaline with ammonia. On heating and subjecting to reduced pressure as before, the gas collected amounted to 18.5 c.c., practically the whole of which was carbon dioxide, only small quantities of nitrogen and oxygen being present.

These two experiments show that attachments of carbon dioxide still cling to the particles of sulphide on settling beneath the surface of the liquid, and after the visible gas bubbles forming the scum have become disengaged. The analysis of the disengaged gas in the previous tests show that it is mainly composed of nitrogen. Assuming that a proportion of oxygen that would give with the nitrogen found a mixture corresponding to atmospheric air, was originally present, the fact that the gas evolved from the sulphides themselves when subjected to reduced pressure is carbon dioxide, shows that the latter is attached more persistently than is the air.

7. An attempt was then made to collect any gas that might be evolved from dry minerals on subjecting them to a low pressure, in the following manner:—The apparatus was an automatic Toepler pump, designed to collect the gas from the apparatus being exhausted.¹ The mineral to be tested was enclosed in a glass flask, and connected with the pump. The pump was then worked until no more gas could be obtained at ordinary temperature, and the last portions of the gas were collected for analysis. The flask containing the mineral was then heated by immersing in a water bath, containing boiling water, the pump being kept continuously working, and the further quantities of gas obtained were collected and analysed.

At first the pump was used with a desiccating apparatus inserted between the flask containing the mineral and the pump, but as the desiccating agent used (phosphorus pentoxide was first tried, and then dehydrated copper sulphate) in each case apparently adsorbed and retained to a greater or lesser extent portion of the gas first evolved, the pump was finally used without the desiccating apparatus, the minerals being previously dried as far as possible by keeping them in a desiccator for several days. The vacuum obtained under these conditions was, however, not so complete as when the desiccating apparatus was used.

Table A shows the results of these tests. Column III. of this table shows the composition of the last portions of gas

¹ "An Automatic Toepler Pump designed to collect the gas from the apparatus being exhausted." Bertram D. Steele, D.Sc., Proc. of Physical Society, London. Vol. xxii.; also Phil. Mag., June, 1910.

TABLE A.—Analysis of gas obtained from dry minerals in *vacuo*.

Mineral taken.	Weight in gms.	Last portion of gas obtained without heating (unit = .0033 c.c.)	Additional gas obtained on heating (unit = .0032 c.c.)
Chalcopyrite (freshly crushed dry lump)	100	25.6 units with the composition of CO ₂ *N 23.8 O 66.4	23.9 units composed of CO ₂ 81.2 *N 17.5 O 1.2
Broken Hill zinciferous tailings	100	11.7 CO ₂ 8.5 N	20.1 CO ₂ 67.6† N 28.8 O 3.4
Zinc concentrates (obtained by oil and acid flo- tation process)	67	37.4 CO ₂ 0.2	4.7 CO ₂ 68 † N 29.8 O 2.1
Broken Hill slimes	100	30.1 CO ₂ 64.1 N 31.8 O 3.9	22.7 CO ₂ 99 †
Broken Hill slimes (from another mine)	58	8.4 CO ₂ 11.9 N 72.6 O 15.4	126 CO ₂ 85 †
Crystalline galena	162	60 CO ₂ 5.1	79.2 CO ₂ 69.4 N 25.7 O 4.8
Rhodomite (cont. a little zinc blende and galena)	98	16.8 CO ₂ 5.3 N 83.9 O 11.9	19.8 CO ₂ 29.8 N 63.6 O 6.6
Quartz sand	77	24.2 CO ₂ 0.8	4.1 CO ₂ 4.8 N 73.1 O 21.9
Cerussite	39	16.5 CO ₂ 5.4	25.6 CO ₂ 7.7†
Calcite	16	53.3 CO ₂ 2.2 N 77.8 O 19.8	2.5 CO ₂ 20

* The residual gas remaining after absorbing the CO₂ and oxygen is taken as being nitrogen in these analyses.

† Dried in desiccator.

obtained before the mineral was heated. As the whole of the gas before heating was not collected, these figures have no relation with the whole of the gas obtained, but simply relate to a final product, the quantity and composition of which depends upon the stage of exhaustion reached when it was collected. Column IV. shows not only the composition, but also the total quantities of the gas obtained from the mineral under these conditions. The volume occupied by the different minerals was approximately the same, except in the case of calcite and cerussite.

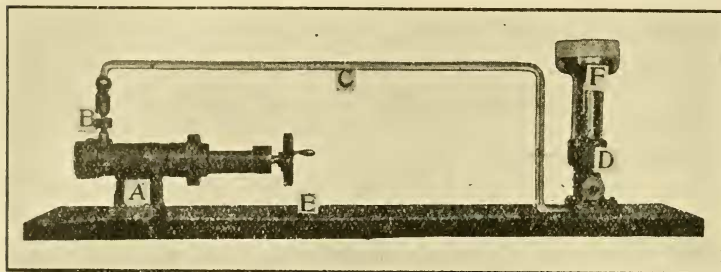
Before each test on the different minerals, the pump was carefully exhausted. As a rule the residual gas from the pump gave negative results—i.e., it was of the same composition as atmospheric air. Some of the blank tests, however, showed the presence of small quantities of carbon dioxide, with a higher proportion of residual gas, after absorbing the oxygen, than would be the case if the gas had been atmospheric air. The blank tests were tried, both in the cold and in heating the empty flask in boiling water. The deviation from the composition of atmospheric air in some of the blank tests may be accounted for by the retention of some of the gas from a previous experiment, on the glass walls of the apparatus or by the mercury itself.

Description of gas analysis apparatus.¹

The gases were analysed in a Bonnier and Mangin gas apparatus (shown in the adjoining text figure), capable of analysing with accuracy very small volumes of gas. The capacity of the apparatus is approximately 0.2 c.c. As can be seen from the reproduced photograph, it consists of a metal cylinder A, from which the mercury can be forced out, or drawn in, from the glass reservoir F, by way of the graduated capillary tube C, and through the large bulb of the capillary tube at B. The movement of the mercury is controlled by means of the small hand wheel E, which moves, on turning, a screw piston, either backwards or forwards, as desired, in the

¹ This gas apparatus was kindly lent by Professor Ewart, of the Botanical Department.

cylinder A. The capillary tube C enters the reservoir F through the base, and rises to a point about level with the bottom of the enlarged diameter of the reservoir at F.



The sample of gas collected from the Toepler pump over mercury in a small test tube is introduced by inserting the test tube over the end of the capillary at F, which is under mercury. The test tube is pushed down until the end of the capillary is in the gas above the mercury. The gas is then drawn into the capillary by working the hand wheel E. The volume of gas is measured on the scale of the capillary tube C. This tube is divided into 60 divisions, subdivided into tenths. Sixty divisions on the scale = 0.2 c.c. The absorbing reagent, such as caustic potash or alkaline pyrogallol, is introduced in the same manner as the sample of gas, and is brought into contact with the latter by turning the small wheel until the liquid reaches the bulb B, after allowing time for the absorption to take place, the gas is pushed back by the mercury and the piston, and the volume again read, the diminution, if any, being noted. D is a screw tap to withdraw the mercury from F.

The results of these tests and analyses show that from the sulphides and material containing sulphides, such as the Broken Hill tailings and slimes, as a rule more gas was obtained than from the calcite and quartz. This gas consisted mainly of carbon dioxide. The residual gas, after absorbing the carbon dioxide and oxygen, was largely in excess of the proportion of nitrogen in atmospheric air, and may contain hydrogen or an excess of argon. That the carbon dioxide in these tests is not

derived from the decomposition of carbonates during the experiment is shown by the negative results shown by cerussite and calcite.

These results indicate that there is apparently a concentration or condensation of gas consisting mainly of carbon dioxide on the surface of the sulphides, and to a much less extent on the other minerals tried. This gas is held persistently, and does not obey the laws of gaseous diffusion, and may therefore be present in the liquid form. This is indicated by the fact that it is the more easily condensed gas, that is the more persistently attached. The fact that finely divided material in the form of slimes will attach more gas than similar material in a coarser state, indicates that the action is a surface action. It may be akin to the action of charcoal, which will absorb large volumes of the more readily condensable gases as carbon dioxide, sulphur dioxide, and ammonia. It is known that water vapour will cling most persistently to some surfaces even at high temperatures.¹

In a previous paper already referred to, the writer found that carbon dioxide was obtained from all the sulphides tried by the aid of heat and exhaustion in the presence of water. It is probable that the gas film can only be expanded for removal in appreciable quantities in the presence of water, and that exhaustion in the dry state does not remove all the gas present. The film can be removed by solvents.

The thickness of the film is probably analogous to the thickness of adsorbed oil and adsorbed water films.

Analogy of gas adsorptions with oil adsorptions.

When an excess of oil is attached to a sulphide it can be separated to some extent by stirring or by pressure. Similarly if a sulphide flotation product, which was floated by gas, is stirred, a large proportion of the excess gas is given off. This can be seen by the larger bubbles bursting, and the shrinkage in volume of the flotation product on standing. If a

¹ "Adsorption of water vapour by quartz." *Journal of Phys. Chem.*, vol. ix., 1905, page 617.

flask is completely filled with some of the flotation product, and the flask is then stoppered, on standing it will be noticed that the scum occupies a lesser volume, partly due to cooling and partly to the bursting of the bubbles and disengagement of the gases. For instance, in a large Winchester quart bottle originally completely filled with the flotation product, on standing the sulphides only occupied about 2 inches on the bottom of the bottle. The remainder of the space (6 inches), except for 5 inches of solution, was occupied by the disengaged gases.

The different stages of oil and gas adsorptions are analogous to a certain extent. In the case of the latter, where there is insufficient gas to buoy the mineral to the surface, but aggregates are formed (such as are brought about by weak chlorine and nitric acid solutions in the cold), there is a similarity to the aggregation stage in oil adsorptions, where a thin secondary film of oil is attached to the primary film. In the case of gaseous aggregations, flotation can be brought about by increasing the amount of attached gas—e.g., by adding a saturated solution of carbon dioxide, the bubbles of the latter gas becoming attached to the aggregates, and buoy them to the surface.

Thus the stages in producing flotation of a sulphide by oil without the aid of gas are:—

- (1) Primary adsorption film.
- (2) Secondary attachments, which will form aggregates.
- (3) Oily magna formed by excess attachments.
- (4) Oil sufficient to bring about the production of magna of such a specific gravity as will float in water.

Similarly the stages gone through in bringing about the flotation of a sulphide with gas are:—

- (1) Primary adsorption film.
- (2) Aggregates formed by secondary attachments.
- (3) Fairly stable aggregates which float by the aid of heat or reduced pressure.

(4) A scum or froth containing an excess of gas, which is mostly disengaged by agitation, after buoying the aggregates to the surface.

Flotation experiments with varying amounts of oil and acid.

The following is a series of flotation experiments carried out with a view to obtaining some data as to the effect of acid on the subsequent flotation product produced when an oil is used, the results of which are given in Table B.

The tests were carried out in an enamelled pot, with a stirring apparatus attached. The pot was heated from below by a gas burner. The method of effecting the flotation was to add the various materials taken in the tests to the 1400 c.c. of water in the pot, and to gradually heat the mixture, at the same time keeping the agitating propeller working continuously. On ceasing the agitation for a few minutes to let the flotation product come to the surface, this latter was skimmed off with a wire gauze strainer. After each skimming another period of agitation was given, and in some cases, as noted in the table, more acid was added, and the flotation product re-skimmed. The tailings called No. 1 have a gangue consisting mainly of quartz and rhodonite, and those called No. 2 have a more calcitic gangue. In the tests numbered 1-10 inclusive, the tailings with the rhodonite gangue were used, and in tests 11-14 inclusive the tailings with the calcite gangue were used. Except where otherwise stated, 1400 c.c. of water were used in each experiment.

The results of the experiments show that (1) without the addition of acid the flotation product produced by oil contains much gangue material, and (2) that the addition of acid up to a certain point decreases the amount of gangue in the flotation product.

This series of experiments was carried out in conjunction with Mr. Donald Clark, late lecturer in Metallurgy at the University.

TABLE B.—*Flotation Experiments.*

No.	Materials taken for test.	Weight of Flotation product in gms.	Containing % Zn.	Containing % insol. gangue.	Weight of residues produced.	Containing % Zn.	Containing % insol. gangue.	Remarks.
1	No. 1 Broken Hill tailings 400 gms. Oleic Acid 0.8 gm.	272	22.4	46.6	119	14.3	39.6	Heated to near boiling point. Agitated repeatedly and skimmed.
2	Water 1400 c.c. Tailings 400 gms. H ₂ SO ₄ , three lots of 8 c.c. each added	129	49.4	1.4	236	6.3	71.4	First 8 c.c. of acid gave little scum, 2nd copious, 3rd poor. Flotation distinct at 80° C.
3	Tailings 400 gms. - H ₂ SO ₄ 5 c.c. - Oleic Acid 0.8 gm. -	93	46.3	1.1	292	11.0	60	
4	Tailings 400 gms. - H ₂ SO ₄ 10 c.c. - Oleic Acid 0.8 gm. -	105	46.8	1.2	276	9.8	69	
5	Tailings 400 gms. - H ₂ SO ₄ 15 c.c. - Oleic Acid 0.8 gm. -	109	48.7	1.4	261	8.3	64.6	
6	Tailings 400 gms. - H ₂ SO ₄ 1 gm. - Oleic Acid 0.4 gm. -	37.5	48	1.8	354	1.9	49.2	Skimmed and stirred about 20 times.
7	Tailings 400 gms. - H ₂ SO ₄ 2 gms. - Oleic Acid 0.4 gm. -	84.5	33	23.2	308.5	17.5	53.6	Skimmed and stirred about 20 times.
8	Same as No. 7 with H ₂ SO ₄ 4 gms. -	78	40.5	3.2	312	14.3	58	
9	Same as No. 7 with H ₂ SO ₄ 8 gms. -	77	47.5	1.2	308	12.7		
10	Same as No. 7 with H ₂ SO ₄ 12 gms. -	80	47.4	1.0	295	12.4	58.6	
11	No. 2 Broken Hill Tailings 400 gms. H ₂ SO ₄ 4 c.c. - Oleic Acid 0.4 gm. -	27.5	36.8	9.0	365	11.4	54.6	
12	Same as No. 11 with H ₂ SO ₄ 8 c.c. -	36	43.7	4.8	351	9.7	62.4	
13	Same as No. 11 with H ₂ SO ₄ 12 c.c. -	78	45.3	2.2	298	5.0	69.6	
14	Same as No. 11 with H ₂ SO ₄ 16 c.c. -	78.5	45.4	0.8	311	4.6	67	

TABLE B.—(Continued).

No.	Materials taken for test.	Weight of Flotation product in gms.	Containing % Zn.	Containing % insol. gangue.	Weight of residue produced.	Containing % Zn.	Containing % insol. gangue.	Remarks.
15—	Broken Hill Slimes 400 gms. water 1500 c.c. H ₂ SO ₄ 7 gms. - Oleic Acid 0.8 gm. -	122	31.5	11.0	277	15.1	34.2	
16—	Same as No 15 but with 14 gms. H ₂ SO ₄	217	32.2	9.0	166	4.8	54.6	Skimmed about 30 times.
17—	Broken Hill tailings 340 gms. - " " slimes 60 gms. - " H ₂ SO ₄ 19.2 c.c. added in 3 lots of 6.4 c.c. each -	1st 38.5 2nd 72	42.9 51.2	2.8 1.0	262	8.4	64.8	The third addition of 6.4 c.c. produced no more flotation.
18—	Same as No. 17 but with Oleic Acid 0.4 gms. H ₂ SO ₄ added in 3 lots of 6 c.c. each -	(1) 75.5 (2) 17.5 (3) 7.5	39.2 46.3 45.7	8.6 2.2 2.4	268	5.8	60.4	
19	Broken Hill tailings 340 gms. - " " slimes 60 gms. - " Fuel oil 1.5 gms. -	(1) 122.5 (2) 25 (3) none	38.2 47.9	10.8 5.1	230	18.8	44.6	
20—	Broken Hill tailings 340 gms. + H ₂ SO ₄ added in three lots of 6 c.c. each - slimes 60 gms. -	(1) 7.2 (2) 22.7	35.4 44.9	10.6 2.2	330	8.3	63.8	
21—	Broken Hill Crude ore 200 gms. - Oleic Acid 0.4 gm. - H ₂ SO ₄ 2.4 c.c. -	(3) 16.8 (4) 8.5 (5) none	45.0 48.4	1.4 1.2	128	6.8	63.2	
22—	Broken Hill Crude ore 200 gms. - Oleic Acid 0.4 gm. -	(1) 57.5 (2) 69.5	20.6 20.8	29.2 30.6	73	10.9	56	1st float 6 skims. Heated gradually to 80° C; 2nd float 15 skims. 20 minutes agitation.

The separation of intimately mixed lead and zinc sulphides.

One of the problems to be overcome in the treatment of lead zinc ores is the separation of the lead and zinc sulphides into suitable products for subsequent treatment. For instance the concentrates from the different flotation processes working at Broken Hill contain varying amounts of zinc blende and galena. When these concentrates have been produced from fairly coarse tailings, a fair separation of the galena and blende can be made by the difference in gravity of the minerals, by such appliances as vanners and concentrating tables. However, with concentrates produced from slime, the separation of the lead and zinc sulphides becomes very much more difficult, and cannot be efficiently effected by gravity concentration. One method that has been used is as follows:—The mixed sulphides are given an oxidising roast at a low temperature, which hardly affects the zinc blende, but which causes a "coat" of lead sulphate to form on the surface of the lead sulphide particles. The product is then treated by a flotation process, the zinc blende floating and the sulphated galena behaving similarly to gangue, and not floating. This is known as the Horwood process.¹

The writer tried various chemical solutions for the purpose of preventing the flotation of the galena in such mixtures of sulphides. Some fairly good results were obtained by using a solution of ferric chloride. The action of the ferric chloride solution is to cause a permanent and not easily detached coat on the particles of galena. The zinc blende is unaffected by the solution. This white coat formed on the surface of the galena particles consists of sulphur and lead chloride. When the ferric chloride solution is used hot, the action is quicker. Some oxide of iron, thrown out of solution, is sometimes present in the substance forming the coat when the ferric chloride is allowed to stand on the mixed sulphides for some time. Any lead being dissolved is re-precipitated by the sulphuric acid in

¹ "Treatment of mixed sulphides by the Horwood process." E. J. Horwood, Proc. Aust. Institute Mining Engineers, June, 1911.

the subsequent flotation operations. The ferric chloride becomes reduced to the ferrous state, and can be readily regenerated if required.

The results of some small tests on various ores and products are as follow :—

Details of ferric chloride tests.

No. 1.—Concentrates produced from an acid flotation on Broken Hill tailings, ground to pass 80 mesh sieve.

Fifty gms. taken and kept in suspension for half an hour, with 200 c.c. water containing 10 gms. FeCl_3 , and allowed to stand 18 hours. Refloated with H_2SO_4 and a small amount of oleic acid.

	Zn. p.c.	Pb. p.c.
Zinc product, 45 gms., floated - -	51.0	6.2
Lead product, 5 gms., not floated -	7.4	47.6

No. 2.—Concentrates produced from an acid flotation on Broken Hill slimes. 200 gms. of the mixed concentrate kept in suspension for 6 hours, with 300 c.c. of a 10 per cent. FeCl_3 solution.

Refloated with sulphuric acid and a small amount of oleic acid.

	Zn. p.c.	Pb. p.c.
Zinc product, 169 gms. - - -	51.8	5.3
Lead product, 28 gms. - - -	16.7	38.1

No. 3.—Concentrates produced from an acid flotation on another sample of Broken Hill slimes. 100 gms. concentrates taken and stood for 24 hours with 300 c.c. 10 per cent FeCl_3 solution.

Refloated with sulphuric and small amount of oleic acid.

	p.c. Zn.	p.c. Pb.	oz. ag.
Zinc product, 67 gms. - -	48.5	8.2	25.25
Lead product, 31.5 gms. -	7.7	46.8	13.25

No. 4.—Crude zinc lead ore from Tasmania. 200 gms. ore kept in suspension for three-quarters hour and then let stand with a 3 per cent. FeCl_3 solution.

Floated the mixed sulphides with a small quantity of H_2SO_4 .

	p.c. Zn.	p.c. Pb.	ozs. per ton Ag.
Zinc product, 77 p.c. by weight	44.8	5.7	22.6
Lead product, 33 p.c. by weight	10.8	41.3	9.4

No doubt these results could be greatly improved upon under better working conditions and by working on a larger scale. For instance, when working with a deeper flotation vessel, the lighter particles in the lead product have a better opportunity to settle, and are not so likely to be carried over mechanically with the flotation product. On refloating the zinc product, more lead can be separated as an unfloatable residue.

The writer wishes to acknowledge the suggestions and advice in this work by Messrs. Donald Clark, A. J. Higgin and T. G. Greenway.
